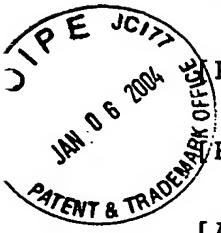


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Kozo OIKAWA

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[Inventor]

[Address]

c/o Nisshinbo Industries, Inc.,
R&D Center,
1-2-3, Onodai, Midori-ku,
Chiba-shi, Chiba-ken, Japan

[Name]

Shun HASEGAWA

[Inventor]

[Address]

c/o Nisshinbo Industries, Inc.,
R&D Center,
1-2-3, Onodai, Midori-ku,
Chiba-shi, Chiba-ken, Japan

[Name]

Gen MASUDA

[Inventor]

[Address]

c/o Nisshinbo Industries, Inc.,
R&D Center,
1-2-3, Onodai, Midori-ku,
Chiba-shi, Chiba-ken, Japan

[Name]

Yukiko YANO

[Inventor]

[Address]

c/o Nisshinbo Industries, Inc.,
R&D Center,
1-2-3, Onodai, Midori-ku,
Chiba-shi, Chiba-ken, Japan

[Name]

Kazuo SAITO

[Inventor]
[Address] c/o Nisshinbo Industries, Inc.,
R&D Center,
1-2-3, Onodai, Midori-ku,
Chiba-shi, Chiba-ken, Japan
[Name] Atsushi HAGIWARA

[Applicant]
[Identification Number] 000004374
[Name] Nisshinbo Industries, Inc.

[Agent]
[Identification Number] 100079304
[Patent Attorney]
[Name] Takashi KOJIMA

[Agent]
[Identification Number] 100103595
[Patent Attorney]
[Name] Yuko NISHIKAWA

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[SPECIFICATION]

[TITLE OF THE INVENTION] Fuel Cell Separator Composition,
Fuel Cell Separator and Method of
Manufacture, and Solid Polymer
Fuel Cell

[CLAIMS]

[Claim 1] A fuel cell separator composition comprising an
electrically conductive carbonaceous powder and a binder,
10 the binder being a mixture of a thermoset resin with a
polyoxazine compound having a plurality of oxazine rings.

[Claim 2] The fuel cell separator composition of claim 1
which contains 5 to 200 parts by weight of the polyoxazine
compound per 100 parts by weight of the thermoset resin.

15 [Claim 3] The fuel cell separator composition of claim 1
or 2 which contains 100 to 6,000 parts by weight of the
conductive carbonaceous powder per 100 parts by weight of
the thermoset resin, the conductive carbonaceous powder
having an average particle size of 10 nm to 500 μm .

20 [Claim 4] The fuel cell separator composition of claim 1,
2 or 3 further comprising up to 500 parts by weight of a
fibrous base per 100 parts by weight of the thermoset resin.

[Claim 5] A fuel cell separator made by imparting to the
fuel cell separator composition of any one of claims 1 to 4
25 a separator shape having gas supplying and removing channels
on one or both sides thereof, which separator, when a 3.5 g
specimen is cut therefrom, placed in 305 ml of deionized
water and heated at 90°C for 500 hours, imparts to the water
an electrical conductivity of not more than 20 $\mu\text{S/cm}$.

30 [Claim 6] The fuel cell separator of claim 5 which has a
resistivity, as measured according to JIS H0602, of at most
50 $\text{m}\Omega\cdot\text{cm}$ and a gas transmission rate, as measured by method
B of JIS K7126, of at most 50 $\text{ml/m}^2\cdot\text{day}\cdot\text{atm}$.

[Claim 7] A method of manufacturing fuel cell separators,
35 comprising the steps of:



preparing a fuel cell separator composition comprising an electrically conductive carbonaceous powder and a binder which is a mixture of a thermoset resin with a polyoxazine compound, and

- 5 shaping the composition into a fuel cell separator having gas supplying and removing channels on one or both sides thereof;

wherein the composition is prepared by the admixture of 100 parts by weight of the thermoset resin, 5 to 200 parts by
10 weight of the polyoxazine compound, 100 to 6,000 parts by weight of the conductive carbonaceous powder, and 0 to 500 parts by weight of a fibrous base.

[Claim 8] A solid polymer fuel cell comprising a plurality of stacked unit cells, each unit cell being comprised of a
15 solid polymer electrolyte membrane, a pair of electrodes disposed on either side of the polymer electrolyte membrane, and a pair of separators disposed on either side of the pair of electrodes such as to form gas supplying and removing channels; wherein at least some of the separators within the
20 fuel cell are fuel cell separators according to claim 5 or 6.

[Claim 9] The solid polymer fuel cell of claim 8 which has an initial voltage V_1 and a voltage V_2 after 200 to 500 hours of continuous operation, such that $(V_2/V_1) \times 100$ is at least
25 80%.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention]

The present invention relates to fuel cell separator
30 compositions and to fuel cell separators made therewith as well as a method of manufacturing such fuel cell separators. The invention also relates to a solid polymer fuel cell assembled using such fuel cell separators as some or all of the separators therein.

[0002]

[Prior Art and the Problem to be Solved by the Invention]

Fuel cells are devices which convert chemical energy directly into electrical energy by placing a pair of electrodes in mutual contact through an intervening electrolyte, feeding a fuel to one of the electrodes and an oxidant to the other electrode, and carrying out oxidation of the fuel electrochemically within the cell. There are several types of fuel cells, depending on the electrolyte used. Solid polymer fuel cells in which the electrolyte is a solid polymer electrolyte membrane have attracted considerable attention recently for their ability to achieve a high energy output.

[0003]

As shown in FIG. 1, such solid polymer fuel cells are composed of a stack of from several tens to several hundreds of unit cells, each unit cell having a pair of fuel cell separators 1, 1 with a plurality of ribs 1a on either side thereof, between which separators 1 are disposed a solid polymer electrolyte membrane 2 and a pair of gas diffusing electrodes (a fuel electrode and an oxidant electrode) 3, 3.

[0004]

In the illustrated solid polymer fuel cell, a stream of hydrogen is supplied to the fuel electrode, a stream of oxygen is supplied to the oxidant electrode, and the electrical current produced by the cell is drawn off by an external circuit. The reactions which take place at the respective electrodes can be represented as follows.

Fuel electrode reaction: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

Oxidant electrode reaction: $2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$ (2)

Overall reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

[0005]

That is, hydrogen (H_2) is converted into protons (H^+) at the fuel electrode. The protons then migrate through the solid polymer electrolyte membrane to the oxidant electrode,

where they react with oxygen (O_2) to form water (H_2O). The supply and removal of reactant and product gases and the drawing off of electrical current are thus essential to operation of the solid polymer fuel cell. Moreover, it is
5 presumed that the solid polymer fuel cell will generally be operated in a wet environment within a temperature range of room temperature to $120^\circ C$, meaning that water will be handled in a liquid state. Arrangements must therefore be made to control the supply of water to the fuel electrode
10 and to remove water from the oxidant electrode.

[0006]

Of the components making up this type of fuel cell, the fuel cell separator, as shown in FIG. 2 (A) and (B), has the distinctive shape of a thin plate provided on one or
15 both sides thereof with a plurality of flow channels 4 for the supply and removal of gases. It plays several important roles, one of which is to separate the fuel gas, oxidant gas, and cooling water flowing through the fuel cell to keep them from mingling. In addition, it transmits from the fuel
20 cell electrical energy generated within the cell, and dissipates out of the fuel cell heat that forms within the cell. Accordingly, a need has been strongly felt for fuel cell separators which, in addition to gas barrier properties, electrical conductivity and corrosion
25 resistance, also have sufficient mechanical strength to resist cracking and breaking of the separators from the tightening of bolts and nuts during fuel cell assembly, and which moreover are endowed with excellent vibration and impact resistance when the fuel cell is used as a mobile
30 power supply for automotive and other similar applications.

[0007]

Carbon composites in which various thermoplastic or thermoset resins offering certain advantages in terms of ease of production and cost are employed as binders have
35 already been proposed for use in solid polymer fuel cell separators of this type. Examples include carbon composites in which the following are used as the binder: the phenolic

and other thermoset resins described in JP-A 59-26907; and the polypropylene, nylon and other thermoplastic resins described in JP-A 56-116277.

[0008]

5 However, fuel cell separators made of carbon composites in which such thermoplastic or thermoset resins are used as the binder, while preferable from the standpoint of production and cost to the separators machined from graphite sheets that were previously used, leave much to be
10 desired in terms of such performance characteristics as mechanical strength, chemical resistance, gas permeability, and dimensional stability. An additional drawback is the need for degassing during the separator molding or forming operation.

15 [0009]

 It is therefore one object of the invention to provide a fuel cell separator composition from which there can be obtained a fuel cell separator that is capable of being mass-produced and has excellent electrical conductivity,
20 mechanical strength, chemical resistance, gas impermeability, low ion extraction, and excellent molding or forming properties. Another object of the invention is to provide a fuel cell separator made from the same fuel cell separator composition. A further object is to provide a
25 method of manufacturing such a fuel cell separator. A still further object is to provide a solid polymer fuel cell which has been assembled using such fuel cell separators as some or all of the separators therein.

[0010]

30 [Means for Solving the Problem and Embodiment of the Invention]

 In order to achieve the above-mentioned objects, we have discovered that fuel cell separator compositions wherein a mixture of a thermoset resin with a polyoxazine
35 compound having a plurality of oxazine rings is employed as the binder for an electrically conductive carbonaceous powder can be molded or formed into fuel cell separators

which have improved high-temperature durability, unlike the prior art wherein use of a binder composed of a thermoplastic or thermoset resin alone results in an inadequate high-temperature durability, and which are also
5 endowed with better mechanical strength, chemical resistance, gas barrier properties and water resistance, lower ion extraction, better dimensional stability, and little or no need for degassing during molding or forming.

[0011]

10 We have also found that solid polymer fuel cells assembled using such separators of excellent electrical conductivity, mechanical strength, chemical resistance, gas impermeability, low ion extraction, and molding or forming properties as some or all of the separators within the fuel
15 cell undergo minimal decline in energy output and have a high operating efficiency, even when the separator has high gas barrier properties and the fuel cell is continuously operated for a long period of time. Hence, such fuel cells are well suited for use as mobile electrical power supplies
20 for such applications as conventional automobiles, hybrid cars and small boats.

[0012]

Accordingly, the present invention provides the following fuel cell separator composition, fuel cell
25 separator and method of manufacture, and solid polymer fuel cell.

Claim 1:

A fuel cell separator composition comprising an electrically conductive carbonaceous powder and a binder,
30 the binder being a mixture of a thermoset resin with a polyoxazine compound having a plurality of oxazine rings.

Claim 2:

The fuel cell separator composition of claim 1 which contains 5 to 200 parts by weight of the polyoxazine
35 compound per 100 parts by weight of the thermoset resin.

Claim 3:

The fuel cell separator composition of claim 1 or 2 which contains 100 to 6,000 parts by weight of the conductive carbonaceous powder per 100 parts by weight of the thermoset resin, the conductive carbonaceous powder having an average particle size of 10 nm to 500 μm .

Claim 4:

The fuel cell separator composition of claim 1, 2 or 3, further comprising up to 500 parts by weight of a fibrous base per 100 parts by weight of the thermoset resin.

Claim 5:

A fuel cell separator made by imparting to the fuel cell separator composition of any one of claims 1 to 4 a separator shape having gas supplying and removing channels on one or both sides thereof, which separator, when a 3.5 g specimen is cut therefrom, placed in 305 ml of deionized water and heated at 90°C for 500 hours, imparts to the water an electrical conductivity of not more than 20 $\mu\text{S/cm}$.

Claim 6:

The fuel cell separator of claim 5 which has a resistivity, as measured according to JIS H0602, of at most 50 $\text{m}\Omega\cdot\text{cm}$ and a gas transmission rate, as measured by method B of JIS K7126, of at most 50 $\text{ml/m}^2\cdot\text{day}\cdot\text{atm}$.

Claim 7:

A method of manufacturing fuel cell separators, comprising the steps of:
preparing a fuel cell separator composition comprising an electrically conductive carbonaceous powder and a binder which is a mixture of a thermoset resin with a polyoxazine compound, and
shaping the composition into a fuel cell separator having gas supplying and removing channels on one or both sides thereof;
wherein the composition is prepared by the admixture of 100 parts by weight of the thermoset resin, 5 to 200 parts by weight of the polyoxazine compound, 100 to 6,000 parts by

weight of the conductive carbonaceous powder, and 0 to 500 parts by weight of a fibrous base.

Claim 8:

A solid polymer fuel cell comprising a plurality of
5 stacked unit cells, each unit cell being comprised of a solid polymer electrolyte membrane, a pair of electrodes disposed on either side of the polymer electrolyte membrane, and a pair of separators disposed on either side of the pair of electrodes such as to form gas supplying and removing
10 channels; wherein at least some of the separators within the fuel cell are fuel cell separators according to claim 5 or 6.

Claim 9:

The solid polymer fuel cell of claim 8 which has an
15 initial voltage V_1 and a voltage V_2 after 200 to 500 hours of continuous operation, such that $(V_2/V_1) \times 100$ is at least 80%.

[0013]

The invention will be described in more detail below.

20 The fuel cell separator composition of the invention is composed primarily of (A) a binder and (B) an electrically conductive carbonaceous powder. The binder (A) is a mixture of (A-1) a thermoset resin and (A-2) a polyoxazine compound having a plurality of oxazine rings.

25 [0014]

Illustrative, non-limiting examples of the thermoset resin (A-1) include phenolic resins (e.g., resoles, novolaks), furan resins (e.g., furfuryl alcohol resins, furfuryl alcohol-furfural resins, furfuryl alcohol-phenol
30 resins), polyimide resins, polycarbodiimide resins, polyacrylonitrile resins, pyrene-phenanthrene resins, polyvinyl chloride resins, epoxy resins, urea resins, diarylphthalate resins, unsaturated polyester resins and melamine resins. These may be used singly or as combination
35 of two or more thereof. Phenolic resins, epoxy resins, or mixtures thereof are especially preferred.

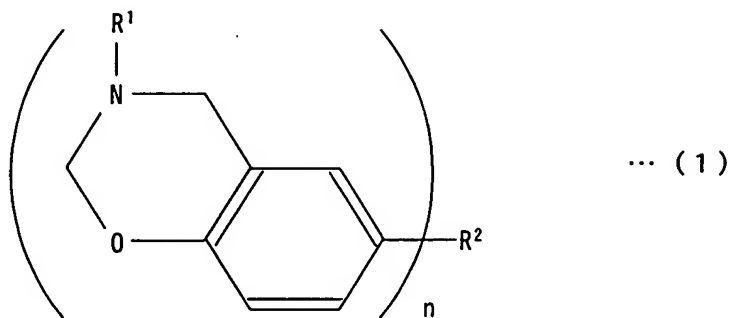
[0015]

The polyoxazine compound having a plurality of oxazine rings (A-2) is preferably a compound of general formula (1) below.

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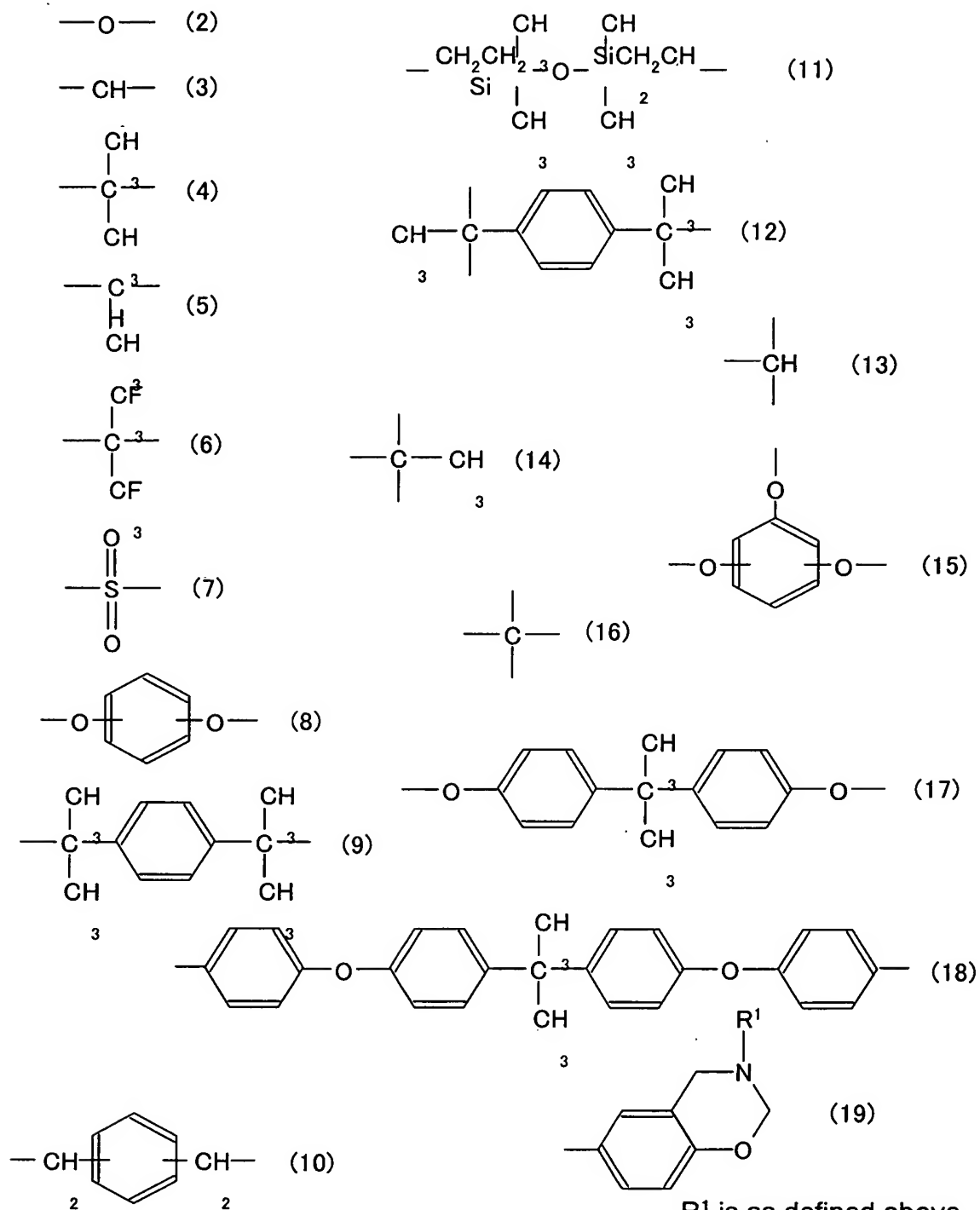
[0016]

[formula 1]



In formula (1), R¹ is an alkyl or aryl group, R² is an organic group of any one of formulas (2) to (19) below, and the letter n is an integer from 1 to 4.

[0017]
[formula 2]



[0018]

In formula (1), R^1 is an alkyl group having 1 to 5 carbon atoms such as methyl or ethyl or an aryl group such as phenyl, tolyl or naphthyl, R^2 is an organic group of any one of formulas (2) to (19) below, and the letter n is an integer from 1 to 4.

[0019]

Such polyoxazine compounds can be prepared by reacting one mole of a polyphenol compound with at least two moles of formalin per phenolic hydroxyl on the phenol compound and an aliphatic or aromatic primary amine (see JP-A 11-256009).

[0020]

Examples of suitable polyphenol compounds include bis(4-hydroxyphenyl)methane (bisphenol F), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), bis(4-hydroxyphenyl)-sulfone (bisphenol S), 1,5-dihydroxynaphthalene and 4,4'-dihydroxybiphenyl.

[0021]

Examples of suitable primary amines include aliphatic amines such as methylamine, ethylamine, butylamine, propylamine and cyclohexylamine, and aromatic amines such as aniline and toluidine.

[0022]

The amount of polyoxazine (A-2) in the composition is preferably 5 to 200 parts by weight, preferably 10 to 150 parts by weight, more preferably 50 to 150 parts by weight, and most preferably 50 to 100 parts by weight, per 100 parts by weight of the thermoset resin (A-1). Too little polyoxazine may lower the strength and gas impermeability of the separator, whereas too much may impart to the molding material an excessive bond strength, which can result in such undesirable effects as poor mold release of the molded article and fouling of the mold.

[0023]

Illustrative examples of the electrically conductive carbonaceous powder (B) in the fuel cell separator composition of the invention include carbon black, acetylene

black, Ketjenblack, flake graphite, lump graphite, artificial graphite, cashew graphite, amorphous carbon and expanded graphite. Any one or combinations of two or more thereof may be used. Of these, flake graphite and
5 artificial graphite are especially preferred.

[0024]

It is desirable for the conductive carbonaceous powder to have an average particle size within a range of preferably 10 nm to 500 μm , and especially 30 to 300 μm . If
10 the carbonaceous powder has an average particle size larger than the above range, the powder may be subjected to size reduction and other suitable particle preparation operations so as to bring the average particle size into the foregoing range. Processes that may be used for this purpose include
15 milling (such as with a mixer, jet mill, ball mill, pin mill, or by a freeze drying technique) and classification (e.g., with a vibrating sieve, Rotex screener, ultrasonic sieve, Micron classifier, or Spedic classifier).

[0025]

20 It is advantageous for the conductive carbonaceous powder to have both an average particle size within the above-indicated range and also the following particle size distribution.

	less than 10 μm :	less than 1 wt%
25	at least 10 μm but less than 700 μm :	50 to 99 wt%
	at least 700 μm :	balance

[0026]

The amount of conductive carbonaceous powder (B) included in the fuel cell separator composition of the
30 invention is preferably 100 to 6,000 parts by weight, more preferably 200 to 2,000 parts by weight, and most preferably 400 to 900 parts by weight, per 100 parts by weight of the thermoset resin (A-1). Too much conductive carbonaceous powder may lower the gas barrier properties and strength of
35 the separator. On the other hand, too little may lower the electrical conductivity.

[0027]

In addition to components (A-1), (A-2) and (B) described above, the fuel cell separator composition may also include, if necessary, optional components for enhancing strength, release properties, hydrolysis resistance, electrical conductivity and other characteristics. Such optional components include fibrous bases, fillers, parting agents, metal powders, and anti-hydrolysis additives.

10 [0028]

Examples of suitable fibrous bases include inorganic fibers such as metal fibers (e.g., iron, copper, brass, bronze, aluminum), ceramic fibers, potassium titanate fibers, glass fibers, carbon fibers, gypsum fibers, rock wool, wollastonite, sepiolite, attapulgite, and synthetic mineral fibers; organic fibers such as aramid fibers, polyimide fibers, polyamide fibers, phenolic fibers, cellulose and acrylic fibers. Any one or combinations of two or more thereof may be used. The fibrous base is typically included in an amount of 0 to 500 parts by weight, preferably 10 to 500 parts by weight, and most preferably 10 to 300 parts by weight, per 100 parts by weight of the thermoset resin (A-1).

[0029]

25 The filler may be a granular organic or inorganic filler. Illustrative examples include silicates such as wollastonite, sericite, mica, clay, bentonite, asbestos, talc and alumina silicate; metal oxides such as alumina, silicon oxide, magnesium oxide, zirconium oxide and titanium oxide; carbonates such as calcium carbonate, magnesium carbonate and dolomite; sulfates such as calcium sulfate and barium sulfate; glass beads, boron nitride, silicon carbide and silica. It is also possible for the filler to be hollow or porous. To increase adhesion of the filler with the thermoset resin within the binder, prior to use the filler may be surface treated with a silane coupling agent, carbodiimide, or any of various suitable emulsions. The

35

amount of filler added is generally from 0 to 500 parts by weight per 100 parts by weight of the thermoset resin (A-1).

[0030]

Non-limiting examples of parting agents that may be used in the inventive composition include silicone-based parting agents, fluorocarbon-based parting agents, parting agents composed of the metal ester of a fatty acid, amide-based parting agents, and wax-based parting agents. Internal parting agents such as carnauba wax, stearic acid, zinc stearate or montanic acid are especially desirable. The amount of parting agent included is generally 0 to 30 parts by weight per 100 parts by weight of the thermoset resin (A-1).

[0031]

Metal powders that may be used in the inventive composition include stainless steel, gold, silver, copper, platinum, titanium, aluminum, and nickel powders. The metal powder has an average particle size of generally about 5 to 30 μm .

[0032]

The fuel cell separator manufacturing method of the invention is a method capable of efficiently producing fuel cell separators having gas supplying and removing channels on one or both sides thereof by molding or forming, with minimal evolution of gases, a composition made up primarily of an electrically conductive carbonaceous powder (B) and a mixture of a thermoset resin (A-1) with a polyoxazine compound (A-2). The composition used for this purpose includes 5 to 200 parts by weight of the polyoxazine compound, 100 to 6,000 parts by weight of the conductive carbonaceous powder, and 0 to 500 parts by weight of a fibrous base per 100 parts by weight of the thermoset resin.

[0033]

Prior to molding, it is advantageous to melt and blend together components (A-1), (A-2) and (B), as well as other optional components such as those described above which may be used as needed. Melting and blending may be carried out

with a suitable apparatus such as a Banbury mixer, rubber roll mill, kneader, single-screw extruder or twin-screw extruder, and at a temperature of 150° C to 450° C.

[0034]

5 Prior to melting and blending, a mixing operation may be carried out using a known mixing means such as a stirring rod, ball mill, sample mixer, static mixer or ribbon blender to further enhance the dispersibility of the thermoset resin, the polyoxazine compound, the conductive carbonaceous
10 powder and the filler.

[0035]

 The resulting fuel cell separator composition of the invention may be employed while still molten in the separator molding or forming step. Alternatively, if
15 necessary, it may be formed into pellets and the pellets dried by a method known to the art, such as fluid bed drying, through-circulation drying with heated air, vacuum drying or vacuum/fluid bed drying.

[0036]

20 The resulting mixture is typically molded with an injection molding machine equipped with a mold capable of molding the mixture into the shape of separators having gas supplying and removing channels on one or both sides thereof.

25 [0037]

 The fuel cell separator manufacturing method of the invention may be carried out using one or a combination of two or more shaping processes selected from among suitable processes known to the prior art, such as injection molding,
30 compression molding, extrusion-compression molding, transfer molding, extrusion, isostatic pressing, belt pressing and roll forming.

[0038]

 The resulting fuel cell separator should preferably
35 meet a level of ion extraction by water. Specifically, when a 3.5 g specimen is cut from the fuel cell separator, placed in 305 ml of deionized water, heated at 90° C, and the

electrical conductivity of the water is measured over time, the water after 500 hours of heating has a conductivity of preferably at most 20 $\mu\text{S}/\text{cm}$, more preferably at most 15 $\mu\text{S}/\text{cm}$, even more preferably at most 10 $\mu\text{S}/\text{cm}$, and most preferably at most 5 $\mu\text{S}/\text{cm}$. Although the conductivity of the water is not subject to any particular lower limit, a conductivity of at least 2 $\mu\text{S}/\text{cm}$ is preferred. If the conductivity of water measured in this way for a fuel cell separator is too large, fuel cells assembled using the separator tend to have a lower energy output and a poor operating efficiency, making it impossible to achieve the desired objects and advantages of the invention.

[0039]

It is advantageous for fuel cell separators of the invention to have a resistivity of at most 50 $\text{m}\Omega\cdot\text{cm}$, preferably at most 30 $\text{m}\Omega\cdot\text{cm}$, and most preferably 2 to 30 $\text{m}\Omega\cdot\text{cm}$, as determined by the four-probe method for measuring silicon single crystal and silicon wafer resistivity described in JIS H0602.

[0040]

It is also advantageous for fuel cell separators of the invention to have the following characteristics, as measured in accordance with JIS K6911 ("Test Methods for Thermoset Plastics") using 100 × 10 × 4 mm test pieces fabricated from the fuel cell separator composition: a flexural strength of 20 to 100 MPa, and preferably 25 to 100 MPa; a flexural modulus of 3.1 to 100 GPa, and preferably 5 to 50 GPa; and a strain of 0.5 to 15 mm, and preferably 0.8 to 12 mm.

[0041]

Moreover, it is desirable for the fuel cell separators of the invention to have a nitrogen transmission rate, as measured at 23°C by method B ("Equal Pressure Method") of JIS K7126 ("Methods for Measuring Gas Transmission Rate through Plastic Film") using a 2 mm thick 100 mm diameter

test piece fabricated from the fuel cell separator composition, of at most 50 ml/m²·day·atm, preferably 30 ml/m²·day·atm, and most preferably 20 ml/m²·day·atm.

[0042]

5 The solid polymer fuel cell of the invention is a plurality of stacked unit cells, each unit cell being composed of a solid polymer electrolyte membrane, a pair of electrodes disposed on either side of the polymer electrolyte membrane, and a pair of separators disposed on
10 either side of the pair of electrodes such as to form gas supplying and removing channels. Some or all of the separators within the fuel cell are the above-described fuel cell separators of the invention.

[0043]

15 Referring to FIG. 1, which illustrates the unit cell construction in a typical solid polymer fuel cell, the fuel cell of the invention is a module composed of a stack of at least several tens of unit cells. Each unit cell is composed of two separators 1, 1, each separator being in the
20 form of a plate having a plurality of ribs 1a on either side thereof which define channels for supplying and removing gases such as hydrogen and oxygen. A solid polymer electrolyte membrane 2 and a pair of gas diffusing electrodes 3, 3 made of carbon paper are sandwiched between
25 the separators 1, 1.

[0044]

At least some of the separators in the inventive fuel cell are the above-described fuel cell separators of the invention which have a high modulus and are highly
30 impervious to gases.

[0045]

Specifically, it is advantageous for at least 50%, preferably 50 to 100%, more preferably 70 to 100%, and most preferably 80 to 100%, of all the separators in the fuel
35 cell to be fuel cell separators according to the invention. If fuel cell separators according to the invention account for too low a proportion of all the separators in the fuel

cell, the energy output by the fuel cell tends to decrease with continuous use over a long period of time, the separators become subject to cracking and breaking due to tightening with bolts and nuts during fuel cell assembly, and the gas sealing properties and impact resistance of the fuel cell have a tendency to decline, making it difficult to achieve the objects and advantages of the invention. Those separators used in the fuel cell which are not fuel cell separators according to the present invention may be separators of a type commonly employed in fuel cells.

[0046]

The solid polymer electrolyte membrane may be of a type which is commonly used in solid polymer fuel cells. Illustrative examples include proton-conducting ion-exchange membranes formed from fluorocarbon resins, such as polytrifluorostyrene sulfonic acids or perfluorocarbon-sulfonic acids bearing the trade name designation Nafion. The surface of the electrolyte membrane is typically coated with a paste composed of a catalyst-supporting carbon powder dispersed in a perfluorocarbonsulfonic acid-containing lower fatty alcohol-water solution (Nafion 117 solution). The catalyst supported by the carbon powder is generally platinum or an alloy of platinum with another metal.

[0047]

The pair of electrodes situated on either side of the solid polymer electrolyte membrane may be made of, for example, carbon paper, carbon felt, or carbon cloth woven from carbon fiber yarn.

[0048]

The electrolyte membrane and electrodes are united by sandwiching the electrolyte membrane between the pair of electrodes and bonding under heat and pressure at 120 to 130°C. Alternatively, the electrolyte membrane and the pair of electrodes may be united by bonding with an adhesive.

[0049]

The resulting electrode/electrolyte membrane/electrode laminate is then mounted between a pair of separators such

as to form flow channels capable of supplying and removing the reactant and product gases, thereby forming a unit cell. Mounting may be carried out by, for example, applying an adhesive to the areas of the separators (i.e., the ribs) which come into contact with the electrodes.

[0050]

By using the high-modulus, highly gas impervious fuel cell separators of the invention as some (preferably at least 50%) or all of the separators in the solid polymer fuel cell of the invention, cracking and breaking does not arise in the separators due to tightening during assembly, and the fuel cell undergoes little decline in energy output and maintains a high operating efficiency during continuous, long-term operation. Moreover, the fuel cell has good gas sealing properties and excellent vibration and impact resistance. This combination of characteristics makes the solid polymer fuel cell of the invention well suited for use as a mobile power supply in such applications as conventional automobiles, hybrid cars and small boats.

[0051]

It is advantageous for the solid polymer fuel cell of the invention to have an initial voltage V_1 and a voltage V_2 after 200 to 500 hours of continuous operation such that the ratio of V_2 to the initial voltage V_1 , or $(V_2/V_1) \times 100$, is at least 80%, preferably at least 90%, and most preferably 95 to 100%. Such a fuel cell undergoes substantially no decline in energy output even when operated continuously for an extended period of time.

[0052]

In addition to being used as a mobile power supply in such applications as conventional automobiles, hybrid cars and small boats, the solid polymer fuel cell of the invention can also be used in a broad range of other applications, including simple power supplies (such as for small-scale local power generation, household power generation and camp sites), and power supplies for satellites and space development.

[0053]

[Effect of the Invention]

Therefore, the present invention enables the efficient mass production, without gas evolution during molding or forming, of fuel cell separators endowed with a high modulus, excellent release properties, dimensional precision and gas impermeability, and low ion extraction. Moreover, by using such fuel cell separators as some or all of the separators in a fuel cell, the invention also makes it possible to obtain high-performance solid polymer fuel cells which undergo little decline in energy output when operated continuously for a long period of time, are not prone to cracking or breaking during assembly, have good gas sealing properties, and are endowed with excellent vibration and impact resistance.

[0054]

[EXAMPLES]

The following Examples and Comparative Examples are provided to illustrate the invention, and are not intended to limit the scope thereof. Note that amounts of the various components shown in Tables 1 to 3 are given in parts by weight.

[0055]

[Examples 1 to 19, Comparative Examples 1 to 5]

In each example, the various components were mixed in the proportions shown in Tables 1 to 3 to form a compound. The resulting compound was charged into a separator mold and compression-molded at 150°C and 1.96 GPa for 5 minutes to produce a fuel cell separator. Each separator had a length of 100 mm, a width of 100 mm and a thickness of 2.0 mm, and had on one or both sides thereof gas supplying and removing channels like those shown in FIG. 2 (A) and (B).

[0056]

The following methods were used to determine the properties of the fuel cell separators thus obtained. The results are shown in Tables 1 to 3.

[0057]

<Bending Tests>

Using an Instron 5544 testing machine and 100 × 10 × 4 mm specimens, the flexural strength and flexural modulus were measured in accordance with JIS K6911 at a support interval of 80 mm and a test rate of 0.5 mm/min.

[0058]

<Resistivity>

The volume resistivity was measured by the four-probe method (JIS H0602) using a Resistivity Processor 2-10 (by NPS Corporation) and a specimen having a diameter of 100 mm and a thickness of 2 mm.

[0059]

<Moldability>

◎: excellent
○: good
△: marginal
×: the composition did not cure

[0060]

<Gas Transmission Rate>

Measurement was carried out using a 2 mm thickness, 100 mm diameter specimen in accordance with Method B ("Isotactic Method") of JIS K7126.

[0061]

<Electrical Conductivity of Water after 500 Hours>

A 3.5 g specimen cut from the fuel cell separator was placed in 305 ml of deionized water, the specimen-containing water was heated to 90°C, and the electrical conductivity of the water over time was measured. The electrical conductivity of the water after 500 hours of heating is shown.

[0062]

Solid polymer fuel cells were assembled by a conventional method using the respective fuel cell separators obtained in Examples 1 to 19 and Comparative Examples 1 to 5. The initial voltage of each polymer fuel

cell was measured, following which the fuel cell was subjected to a 200-hour continuous power generation test. The fuel cell voltage was then measured again, based on which the voltage drop ratio was computed. The results are shown in Tables 1 to 3.

[0063]

[Table 1]

Component (pbw)	Example									
	1	2	3	4	5	6	7	8	9	10
Thermoset resin	100	100	100	100	100	100	100	100	100	100
Polyoxazine compound	10	50	100	150	200	10	200	100	100	100
Flake graphite	470	640	860	1,070	1,280	260	5,000	3,800	2,710	1,800
Flexural strength (MPa)	40	44	47	45	41	40	40	47	50	53
Flexural modulus (GPa)	37	37	38	37	38	38	38	40	38	35
Resistivity (mΩ·cm)	30	23	20	21	30	30	10	6	8	9
Moldability	○	◎	◎	◎	○	○	○	◎	◎	◎
Gas transmission rate(ml/m ² ·day·atm)	20	6	5	5	6	10	10	28	24	16
Conductivity of water after 500 hrs (μS/cm)	2.0	0.8	0.7	0.8	2.0	5.0	2.5	2.5	2.1	1.8
Voltage drop ratio (%)	99	99	98	98	99	99	99	99	98	98

* Thermoset resin: novolak-type phenolic resin

* Polyoxazine compound: B-a type benzoxazine (made by Shikoku Chemicals Corporation)

[0064]

[Table 2]

Component (pbw)	Example								
	11	12	13	14	15	16	17	18	19
Thermoset resin	100	100	100	100	100	100	100	100	100
Polyoxazine compound	100	100	100	100	100	100	100	100	100
Flake graphite	1,340	1,133	710	600	860	860	860	860	860
Carbon fibers	-	-	-	-	32	53	106	160	212
Flexural strength (Mpa)	47	49	50	52	48	56	60	54	48
Flexural modulus (Gpa)	37	38	38	37	38.5	39	40	42	43
Resistivity (mΩ·cm)	12	16	19	22	21	23	26	28	34
Moldability	◎	◎	◎	◎	◎	◎	○	○	○
Gas transmission rate(ml/m ² ·day·atm)	15	16	19	19	5	10	12	18	25
Conductivity of water after 500 hrs (μS/cm)	1.5	1.7	1.9	2.1	1.5	1.7	1.8	1.9	2.0
Voltage drop ratio (%)	99	98	97	96	99	99	98	95	90

* Thermoset resin: novolak-type phenolic resin

* Polyoxazine compound: B-a type benzoxazine (made by
Shikoku Chemicals Corporation)

[0065]

[Table 3]

	Comparative Example				
	1	2	3	4	5
Thermoset resin	100	100	100	100	100
Polyoxazine compound	5	500	100	100	100
Flake graphite	450	2,560	50	9,000	860
Carbon fibers	-	-	-	-	1,000
Flexural strength (MPa)	20	25	50	4	10
Flexural modulus (GPa)	37	37	42	10	10
Resistivity (mΩ·cm)	30	40	1,000	50	100
Moldability	×	×	○	×	×
Gas transmission rate (ml/m ² ·day·atm)	1,000	1,200	10	10,000	20,000
Conductivity of water after 500 hrs (μS/cm)	40	30	2	20	50
Voltage drop ratio (%)	50	55	30	3	3

* Thermoset resin: novolak-type phenolic resin

* Polyoxazine compound: B-a type benzoxazine (made by Shikoku Chemicals Corporation)

[BRIEF DESCRIPTION OF THE DRAWING]

[Fig. 1]

Fig. 1 shows a perspective view showing one example of the fuel cell.

[Fig.2]

FIG. 2 shows perspective views of fuel cell separators according to different embodiments of the invention. In (A), gas supplying and removing channels are provided on both sides of the separator. In (B), gas supplying and removing channels are provided on only one side of the separator.

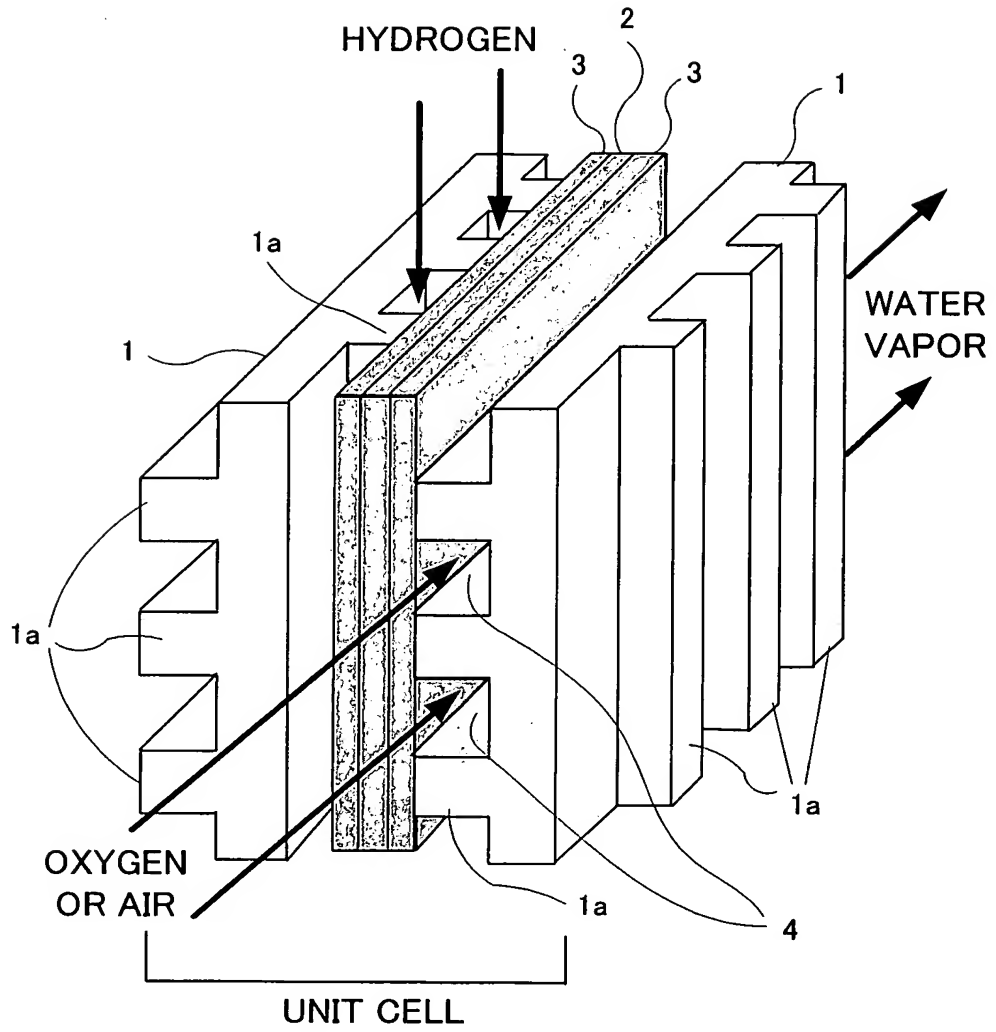
[Explanation of Symbols]

- | | | |
|---|----|---|
| | 1 | Separator |
| | 1a | Rib |
| | 2 | Electrolytic membrane of solid high polymer |
| 5 | 3 | Gas diffusion electrode |
| | 4 | Gas supplying and removing channels |

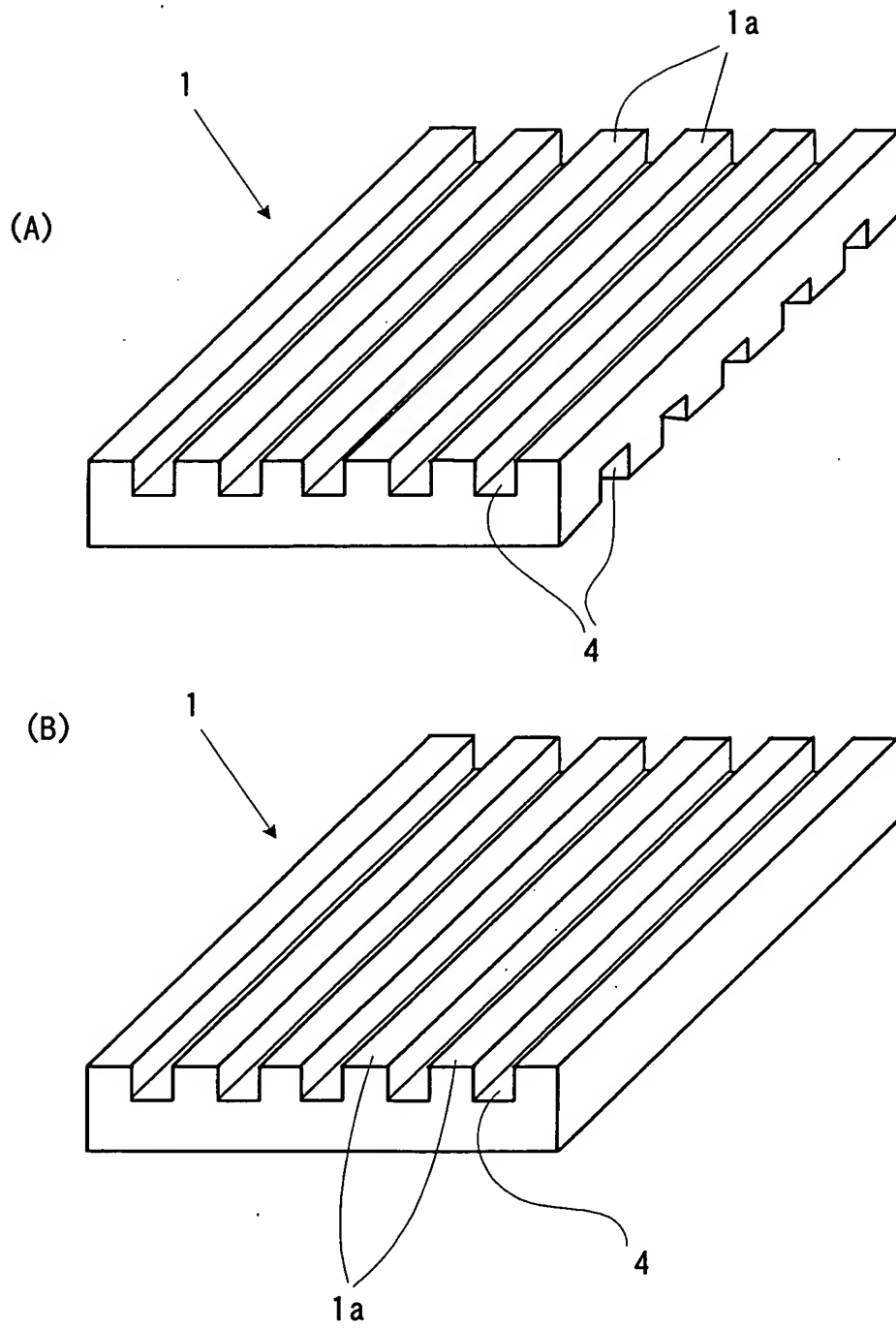
2001-057587

[DRAWING]

[FIG. 1]



[FIG. 2]



2001-057587

[ABSTRACT]

[Means for Solving the Problem]

A fuel cell separator composition containing an electrically conductive carbonaceous powder and a binder that is a mixture of a thermoset resin with a polyoxazine compound having a plurality of oxazine rings can be used to efficiently mass-produce high-modulus fuel cell separators of excellent dimensional stability and gas impermeability.

[Effect]

By employing such fuel cell separators as some or all of the separators in a solid polymer fuel cell, there can be obtained solid polymer fuel cells which are not subject to cracking or breakage during assembly, have good gas sealing properties, and are endowed with excellent vibration and impact resistance.

[Selected Drawing] FIG. 2

SEPARATOR FOR FUEL CELLS OF SOLID POLYELECTROLYTE TYPE AND PROCESSES OF THE PRODUCTION THEREOF

Patent Number: ☐ [EP0784352](#), [A4](#), [B1](#)
Publication date: 1997-07-16
Inventor(s): SAITO KAZUO (JP); TANNO FUMIO (JP); HAGIWARA ATSUCHI (JP)
Applicant(s): NISSHIN SPINNING (JP)
Requested Patent: ☐ [WO9702612](#)
Application Number: EP19960922230 19960704
Priority Number(s): WO1996JP01859 19960704; JP19950194333 19950705
IPC Classification: H01M8/02
EC Classification: [H01M8/02C2C](#), [C04B35/536](#)
Equivalents: CA2198496, DE69611778D, DE69611778T
Cited Documents: [JP62265109](#); [JP58053167](#)

Abstract

A separator for fuel cells of solid polyelectrolyte type which overcomes the disadvantages of the prior art, is lightweight, can be slotted easily, and exhibits high gas barrier properties; and processes for the production thereof. The separator is of the type to be sandwiched between gas diffusion electrodes of the fuel cell and characterized by being made of the carbonaceous composite material comprising expanded graphite particles which have a mean particle diameter of 5 to 12 μm and at least 80 % of which have diameters falling within the range of 0.1 to 20 μm and a thermoplastic or thermosetting resin or a sinter thereof, wherein the graphite particles are dispersed in the resin or sinter thereof, and having slots for feeding oxidant gas or fuel gas on one or both surfaces thereof. The separator can be produced by mixing a thermoplastic or thermosetting resin with the above-specified expanded graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 DEG C and forming slots of feeding oxidant gas or fuel gas on one or both surfaces of the resulting carbonaceous composite material, or by mixing a thermosetting resin with the above graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 DEG C, firing the resulting molding in a nonoxidizing atmosphere at 700 to 3000 DEG C to form a carbonaceous composite material, and forming slots for feeding oxidant gas or fuel gas on one or both surfaces of the material, or by mixing a thermosetting resin with the above graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 DEG C, forming slots for feeding oxidant gas or fuel gas on one or both surfaces of the obtained molding, and firing the resulting slotted molding in a nonoxidizing atmosphere at 700 to 3000 DEG C.



(51) 国際特許分類6 H01M 8/02	A1	(11) 国際公開番号 WO97/02612 (43) 国際公開日 1997年1月23日(23.01.97)
(21) 国際出願番号 PCT/JP96/01859 (22) 国際出願日 1996年7月4日(04.07.96) (30) 優先権データ 特願平7/194333 1995年7月5日(05.07.95) JP (71) 出願人 (米国を除くすべての指定国について) 日清紡績株式会社(NISSHINBO INDUSTRIES, INC.)(JP/JP) 〒103 東京都中央区日本橋人形町2丁目31番11号 Tokyo, (JP) (72) 発明者: および (75) 発明者/出願人 (米国についてのみ) 斉藤一夫(SAITO, Kazuo)(JP/JP) 萩原 敦(HAGIWARA, Atsushi)(JP/JP) 丹野文雄(TANNO, Fumio)(JP/JP) 〒123 東京都足立区西新井栄町1-18-1 日清紡績株式会社 東京研究センター内 Tokyo, (JP) (74) 代理人 弁理士 小林雅人(KOBAYASHI, Masato) 〒162 東京都新宿区神楽坂4丁目3番地 煉瓦塔ビル5階 Tokyo, (JP)		(81) 指定国 CA, JP, US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). 添付公開書類 国際調査報告書
(54)Title: SEPARATOR FOR FUEL CELLS OF SOLID POLYELECTROLYTE TYPE AND PROCESSES OF THE PRODUCTION THEREOF (54)発明の名称 固体高分子電解質型燃料電池用セパレータ及びその製造方法 (57) Abstract A separator for fuel cells of solid polyelectrolyte type which overcomes the disadvantages of the prior art, is lightweight, can be slotted easily, and exhibits high gas barrier properties; and processes for the production thereof. The separator is of the type to be sandwiched between gas diffusion electrodes of the fuel cell and characterized by being made of the carbonaceous composite material comprising expanded graphite particles which have a mean particle diameter of 5 to 12 µm and at least 80 % of which have diameters falling within the range of 0.1 to 20 µm and a thermoplastic or thermosetting resin or a sinter thereof, wherein the graphite particles are dispersed in the resin of sinter thereof, and having slots for feeding oxidant gas or fuel gas on one or both surfaces thereof. The separator can be produced by mixing a thermoplastic or thermosetting resin with the above-specified expanded graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 °C and forming slots of feeding oxidant gas or fuel gas on one or both surfaces of the resulting carbonaceous composite material, or by mixing a thermosetting resin with the above graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 °C, firing the resulting molding in a nonoxidizing atmosphere at 700 to 3000 °C to form a carbonaceous composite material, and forming slots for feeding oxidant gas or fuel gas on one or both surfaces of the material, or by mixing a thermosetting resin with the above graphite particles, pressure-molding the obtained mixture at ordinary temperature to 400 °C, forming slots for feeding oxidant gas or fuel gas on one or both surfaces of the obtained molding, and firing the resulting slotted molding in a nonoxidizing atmosphere at 700 to 3000 °C.		

(57) 要約

従来技術の欠点を克服し、軽量で溝加工を容易に施すことができ、しかも高いガスバリア性を有する固体高分子型燃料電池用セパレータ及びその製造方法を提供することを目的とする。

本発明の固体高分子電解質型燃料電池セパレータは、燃料電池のガス拡散電極間に挟まれる固体高分子電解質型燃料電池用セパレータであって、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物よりなり、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物中に膨張黒鉛粉末が分散されている炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成したことを特徴とし、同じく本発明の固体高分子電解質型燃料電池用セパレータの製造方法は、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂又は熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形して得られた炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成することを特徴とするか、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形した後、該成形物を、非酸化性雰囲気下、 $700^{\circ}\text{C}\sim 3000^{\circ}\text{C}$ で焼成して得られた炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成することを特徴とするか、或いは、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形した後、該成形物の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成し、非酸化性雰囲気下、 $700^{\circ}\text{C}\sim 3000^{\circ}\text{C}$ で焼成することを特徴とする。

情報としての用途のみ

PCTに基づいて公開される国際出願をパンフレット第一頁にPCT加盟国を同定するために使用されるコード

AL	アルバニア	DE	ドイツ	LI	リヒテンシュタイン	PL	ポーランド
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CN	中国	KP	朝鮮民主主義人民共和国	NL	オランダ	UG	ウガンダ
CU	キューバ	KR	大韓民国	NO	ノルウェー	US	アメリカ合衆国
CZ	チェッコ共和国	KZ	カザフスタン	NZ	ニュージーランド	UZ	ウズベキスタン
						VN	ヴェトナム

明 細 書

固体高分子電解質型燃料電池用セパレータ及びその製造方法

5 技術分野

本発明は、固体高分子電解質型燃料電池用セパレータとその製造方法に関するものである。

背景技術

- 10 燃料電池は、資源の枯渇に留意する必要がある化石燃料を使う必要がほとんどない上に、発電に際し騒音をほとんど発生せず、エネルギーの回収率も他のエネルギー発電機関と比べて高くできる等の優れた特徴を持つために、ビルや工場における比較的小型の発電プラントとして開発が進められている。

- 中でも、固体高分子型燃料電池は、他のタイプの燃料電池と比べて低温で作
15 動するので、電池を構成する部品の腐食の問題がなく、従って材料面での腐食の心配が少なく、且つ、低温作動の割には比較的大電流を放電できるといった特徴を持ち、車載用の内燃機関の代替電源として注目を集めている。

- この固体高分子型燃料電池を構成する部品の中で、セパレータは、燃料電池
セルへ流入する反応ガスの流通路を確保すると共に、燃料電池セルで発電した
20 電気を外部へ伝達したり、燃料電池セルで生じた熱を放熱するという役割を担

っており、従って、この固体高分子型燃料電池用セパレータは、前述した役割を果たすために、軽量性、高ガスバリア性、溝加工を行う際の易切削性が求められている。

従来、固体高分子型燃料電池セパレータに用いられている材料は、加工性、

- 5 材料の価格の面からグラファイト材料にフェノール樹脂等の樹脂を含浸したもの、或いは、グラファイト表層にガラス状カーボン層を被覆したものが用いられている。

しかしながら、この樹脂を含浸したグラファイト材料は、ある程度のガスバリア性を得るために、何度も含浸→乾燥の工程を繰り返すことが必要となって

- 10 高価なものになるばかりか、グラファイトを用いているために密度が高く、電池全体の重量が大きくなるという問題点を有している。

又、グラファイト表層にガラス状カーボン層を被覆したものは、上記の場合と同様に何度も含浸→乾燥を繰り返した後、非酸化性雰囲気下で焼成するため、工程が複雑になり、高価なものになったり、或いは、グラファイトを用いてい

- 15 るために密度が高く、電池全体の重量が大きくなる問題点を有する。

又、リン酸型燃料電池で用いられているように、ガラス状炭素を用いることも考えられ、確かに、ガラス状炭素はグラファイトよりは密度が低いために電池全体の重量は軽くなるものの、高価であり、そしてガラス状カーボンは脆性材料であるために、溝加工を施すことが非常に困難で、且つ、加工費が高価に

- 20 なるという問題点がある。

このため、軽量で溝加工を容易に施すことができ、しかも高いガスバリア性を有する固体高分子型燃料電池用セパレータの開発が望まれていた。

- 本発明は、上記課題を解決して、軽量で溝加工を容易に施すことができ、しかも高いガスバリア性を有する固体高分子型燃料電池用セパレータ及びその製造方法を提供することを目的としてなされた。
- 5

発明の開示

- 上記目的を解決するために本発明が採用した固体高分子電解質型燃料電池セパレータの構成は、燃料電池のガス拡散電極間に挟まれる固体高分子電解質型
- 10 燃料電池用セパレータであって、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物よりなり、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物中に膨張黒鉛粉末が分散されている炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成したことを特徴とする
- 15 ものである。

- 又、同じく上記目的を解決するために本発明が採用した固体高分子電解質型燃料電池用セパレータの製造方法の構成は、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂又は熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の
- 20 温度下で加圧成形して得られた炭素複合材料の片面又は両面に、酸化剤ガス又

は燃料ガス供給溝を形成することを特徴とする。

更に又、同じく上記目的を解決するために本発明が採用した固体高分子電解質型燃料電池用セパレータの製造方法の別の構成は、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属

- 5 する膨張黒鉛粉末と、熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形した後、該成形物を、非酸化性雰囲気下、 $700^{\circ}\text{C}\sim 3000^{\circ}\text{C}$ で焼成して得られた炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成することを特徴とするか、或いは、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張
- 10 黒鉛粉末と、熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形した後、該成形物の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成し、非酸化性雰囲気下、 $700^{\circ}\text{C}\sim 3000^{\circ}\text{C}$ で焼成することを特徴とするものである。

- 即ち、本発明者らは、上記目的を達成するために鋭意研究の結果、特定の粒径を有する膨張黒鉛を、熱可塑性樹脂又は熱硬化性樹脂と混合した場合、非常
- 15 に優れた樹脂との混合性を与えるために、成型あるいは賦形した際、軽量で優れたガスバリア性と溝加工性を有する固体高分子電解質型燃料電池用セパレータをもたらすのではないかという発想を得、更に研究を重ねた結果、本発明を完成したものである。

発明を実施するための最良の形態

以下に本発明を説明する。

本発明で使用する膨張黒鉛として、その原料については特に限定されること
5 はなく、例えば天然黒鉛、熱分解黒鉛、キッシュ黒鉛等、通常の膨張黒鉛の製造に用いられるあらゆるものを使用することができる。

上記原料黒鉛から膨張黒鉛を製造するには、従来周知の方法によることができ、例えば、硫酸と過酸化水素とを混合することによりペルオキソー硫酸を生成させた後、このようにして調製された混合液を攪拌しながら原料黒鉛を投入
10 し、約1時間から1日反応させ、この反応させた黒鉛を、不活性ガス中で500℃～1000℃に加熱すればよいのである。

尚、本発明で使用する膨張黒鉛としては、上記のように、濃硫酸と過酸化水素により膨張黒鉛を製造する際に、酸化剤として、過塩素酸、過塩素酸塩、ペルオキシ二硫酸水素アンモニウムから選ばれる少なくとも1種類を添加して処理することにより得られたもの（特開平6-16406号公報参照）であつてもよい。具体的には、95wt%の硫酸320重量部と62%の過酸化水素4重量部との混合物に、ペルオキシ二硫酸水素アンモニウム15%を添加して、
20℃以下に冷却しながら混合し、この混合液に天然黒鉛を投入した後、24時間反応させ、この反応物を窒素ガス中1000℃まで焼成して得た膨張黒鉛
20 である。

上記のようにして得られた膨張黒鉛は粉碎され、必要に応じ所定の粒度及び粒径にそろえられるのであり、本発明で使用する膨張黒鉛は、平均粒径が $5\mu\text{m}$ ～ $12\mu\text{m}$ で、しかも粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}$ ～ $20\mu\text{m}$ の範囲に属するものでなければならない。

- 5 本発明で使用する膨張黒鉛の平均粒径が $5\mu\text{m}$ より小さい場合には、熱可塑性樹脂又は熱硬化性樹脂が膨張黒鉛の粒子間に浸透することが困難となり、そのためにガスバリア性が大きく損われてしまい、逆に平均粒径が $12\mu\text{m}$ より大きい場合には、熱可塑性樹脂又は熱硬化性樹脂が膨張黒鉛の粒子間を埋めることが困難となり、そのためにガスバリア性が大きく損なわれてしまうばかりか、充填密度が落ちて電氣的接続が十分でなくなり、導電性が低下してしまう。

- 更に、本発明で使用する膨張黒鉛は、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}$ ～ $20\mu\text{m}$ の範囲に属する必要がある。即ち、粉碎され、必要に応じ所定の粒度及び粒径にそろえられた膨張黒鉛は、一般的には平均粒径をピークとする粒度分布を有しているが、本発明では、粉末全粒子の粒度測定した場合に、その80%以上が $0.1\mu\text{m}$ ～ $20\mu\text{m}$ の範囲に属し、 $0.1\mu\text{m}$ 以下及び $20\mu\text{m}$ 以上の範囲に属する粒子が20%未満となっている必要があるのである。

- もちろん、本発明で使用する膨張黒鉛粉末は、粉末全粒子の100%の粒径が $0.1\mu\text{m}$ ～ $20\mu\text{m}$ の範囲に分布していてもよく、 $0.1\mu\text{m}$ ～ 20μ

mの範囲内で、更に狭い範囲内に分布していてもよい。

粒度分布のピークが低くなったり、いずれかの方向に移動すると、 $0.1 \mu\text{m}$ 以下及び $20 \mu\text{m}$ 以上の範囲に属する粒子の双方（前者の場合）或いは一方（後者の場合）の数が増加するが、 $0.1 \mu\text{m}$ 以下の粒子の数が増加すると膨

- 5 張黒鉛粉末の表面積が増加し、これにより膨張黒鉛粉末間の樹脂の厚みが小さくなるので、得られるセパレータのガスバリア性が低下してしまい、又、 $20 \mu\text{m}$ 以上の粒子の数が増加すると、粒子の一部が得られるセパレータの表面に露出してしまう可能性が生じるばかりか、膨張黒鉛粉末間に形成される樹脂の層の数が少なくなるので、やはりセパレータのガスバリア性が低下してしまい、
- 10 いずれも好ましくない。

尚、上記膨張黒鉛を粉砕する方法は、従来公知のいずれの方法によってもよく、例えば、ミキサー、ジェットミル、ボールミル、ピンミル、凍結粉砕等の粉砕方法を挙げることができ、前記所定の粒度、粒径にそろえる方法としては、振動ふるい、ローテックススクリーナー、音波ふるい、マイクロクラシファ

- 15 イアー、スベディッククラシファイアー等の分級方法を挙げることができる。

又、本発明で用いられる熱可塑性樹脂としては、ポリエチレン、ポリスチレン、ポリプロピレン、ポリメタクリル酸メチル、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエーテルスルホン、ポリカーボネート、

- ポリオキサメチレン、ポリアミド、ポリイミド、ポリアミドイミド、ポリビニ
20 ルアルコール、ポリビニルクロライド、フッ素樹脂、ポリフェフェニールサル

フォン、ポリエーテルエーテルケトン、ポリスルフォン、ポリエーテルケトン、ポリアリレート、ポリエーテルイミドやポリメチルベンデン等の周知の樹脂を挙げる事ができ、特に限定はされない。

- 一方、本発明で用いられる熱硬化性樹脂としては、ポリカルボジイミド樹脂、
- 5 フェノール樹脂、フルフリルアルコール樹脂、セルロース、エポキシ樹脂、尿素材脂、メラミン樹脂等の周知の樹脂を挙げる事ができ、特に限定はされない。

上記の熱可塑性樹脂或いは熱硬化性樹脂は、粉末状あるいは適当な溶媒に溶かして溶液状にして使用してもよい。

- 10 本発明のセパレータを製造するには、以下に説明する本発明の製造方法によって、まず、その主成分たる膨張黒鉛粉末と樹脂を複合することにより製造される。

- 即ち、最初に前記膨張黒鉛粉末と樹脂とを混合分散して混合物を得るのであり、この混合工程は、通常の工業的な混合方法、例えば、攪拌棒、ニーダー、
- 15 ポールミル、サンプルミル、ミキサー、スタティックミキサー、リボンミキサー等による方法を採用することができる。

- 上記膨張黒鉛と樹脂との量比は、目的とするセパレータの物性等により決定すればよいが、例えば、膨張黒鉛粉末 100 重量部に対して、樹脂を 10 重量部～1000 重量部という範囲を挙げる事ができる。尚、樹脂がこの範囲より
- 20 小さい場合には、セパレータの強度が低くなったり、不浸透性が低下すると

いう問題が起き、又、この範囲より大きい場合には、導電性が不足するという問題が起こる。

次に、この混合物に圧力を加え、樹脂を膨張黒鉛粉末間に行き渡らせることによって成形し、本発明のセパレータのための炭素複合材料とするのであって、

- 5 この成形工程は、加圧成形、静水圧成形、押し出し成形、トランスファー成形、射出－圧縮成形、射出成形、ベルトプレス、プレス加熱、ロールプレス等の従来公知の方法によって行うことができる。尚、この時点で所望の形状に成形しても、この成形工程の前に、前記混合物に溶媒を加えることにより、例えば、
20 μm ～2 mmの径に造粒し、成形性を高めてもよい。

- 10 成型温度については、使用する樹脂に応じて選択すればよいが、常温～400℃を挙げることができる。尚、この成型物を化学的に安定化させるために、さらに成型後に熱処理を行ってもよい。

前記炭素複合材料を使用して本発明のセパレータを製造するには、ガス拡散電極へ酸化剤ガス又は燃料ガスを当該ガス拡散電極の全面に供給するための、

- 15 酸化剤ガス又は燃料ガスの供給溝を設ける必要があり、この溝の形状やサイズ等については、目的とする燃料電池の性能等に合わせ、適宜に設定することができる。

上記混合物の内、熱硬化性樹脂と膨張黒鉛の混合物に関しては、非酸化性雰囲気下で焼成することができる。焼成温度としては、非酸化性ガス中で700℃

- 20 ～3000℃、好ましくは1000℃～2500℃という範囲を例示すること

ができ、700℃より低い焼成温度では、前述の非焼成型成型体と比べて導電性が飛躍的に向上しないという問題があり、3000℃より高い温度は、焼成炉の消耗が著しくなり現実的な生産に適さないという問題点がある。

上記酸化剤ガス又は燃料ガス供給溝を形成するには、熱可塑性樹脂を使用し

- 5 た場合でも熱硬化性樹脂を使用した場合でも、予め金型を供給溝が形成されるように設計しておいたり、或いは、前記炭素複合材料を製造した後に機械加工等の方法で供給溝を形成したりすればよい。

以下実施例によって本発明を更に詳しく説明する。

実施例 1

- 10 平均粒径が7 μm で、粉末全粒子の内の80%以上の粒径が0.1 μm ～20 μm の範囲に属する膨張黒鉛と、ポリカルボジイミド樹脂を表1に示す組み合わせで混合し、150℃、100 kg/cm^2 の圧力で成型品を製造し、この成型品に対し溝加工を施して固体高分子電解質型燃料電池用セパレータを製造した後、その密度、ガス透過率、溝加工性を測定した。密度は、この成型品
- 15 から40mm角、厚さ2mmの板材を切り出し、体積と重量より算出し、又、ガス透過性は、120mm角、厚さ1mmの板材を切り出し、JIS 7126 差圧法によって窒素ガスのガス透過性を測定し、更に、溝加工性は、120mm角、厚さ2mmの板を用意して、深さ1mm、幅5mmの溝を機械加工によって切削し、その外観を観察した。結果を表1に示す。

表 1

		実施例		
		1-1	1-2	1-3
焼成条件		なし	なし	なし
膨張黒鉛		100	100	100
樹脂	ポリカルボジイミド	10	100	1000
	フェノール			
	ポリプロピレン			
	ポリテトラフロロエチレン			
密度		1.2	1.34	1.5
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)		1×10^{-2}	1×10^{-5}	1×10^{-7}
溝加工性		良好	良好	良好

実施例 2

- 実施例 1 と同様の膨張黒鉛とフェノール樹脂を表 2 に示す組み合わせで混合
- 5 し、 150°C 、 100 kg/cm^2 の圧力で成型品を作った。この成型品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 2 に示す。

表 2

		実施例		
		2-1	2-2	2-3
焼成条件		なし	なし	なし
膨張黒鉛		100	100	100
樹脂	ポリカルボジイミド			
	フェノール	10	100	1000
	ポリプロピレン			
	ポリテトラフロロエチレン			
密度		1.16	1.29	1.46
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)		1×10^{-2}	5×10^{-4}	6×10^{-6}
溝加工性		良好	良好	良好

実施例 3

- 実施例 1 と同様の膨張黒鉛とポリプロピレンを表 3 に示す組み合わせで混合
- 5 し、 180°C 、 100 kg/cm^2 の圧力で成型品を作った。この成型品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 3 に示す。

表 3

		実施例		
		3-1	3-2	3-3
焼成条件		なし	なし	なし
膨張黒鉛		100	100	100
樹脂	ポリカルボジイミド			
	フェノール			
	ポリプロピレン	10	100	1000
	ポリテトラフロロエチレン			
密度		1.05	1.12	1.07
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)		2×10^{-2}	2×10^{-4}	2×10^{-7}
溝加工性		良好	良好	良好

実施例 4

実施例 1 と同様の膨張黒鉛とポリテトラフロロエチレンを表 4 に示す組み合

- 5 わせで混合し、 330°C 、 100 kg/cm^2 の圧力で成型品を作った。この成型品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 4 に示す。

表 4

		実施例		
		4-1	4-2	4-3
焼成条件		なし	なし	なし
膨張黒鉛		100	100	100
樹脂	ポリカルボジイミド			
	フェノール			
	ポリプロピレン			
	ポリテトラフロロエチレン	10	100	1000
密度		1.06	1.11	1.13
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)		1×10^{-3}	2×10^{-5}	2×10^{-7}
溝加工性		良好	良好	良好

実施例 5

- 実施例 1 のうち、実施例 1-2 に示される組成（膨張黒鉛／ポリカルボジイミド樹脂＝100 重量部／100 重量部）を実施例 1 と同条件で成型し、これを表 5 に示す温度まで不活性ガス雰囲気下で焼成した。この焼成品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 5 に示す。

表 5

		実施例		
		5-1	5-2	5-3
焼成条件		1000	2000	2500
膨張黒鉛		100	100	100
樹脂	ポリカルボジイミド	100	100	100
	フェノール			
	ポリプロピレン			
	ポリテトラフロロエチレン			
密度		1.38	1.42	1.3
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)		8×10^{-6}	2×10^{-6}	8×10^{-6}
溝加工性		良好	良好	良好

比較例 1

平均粒径が $100 \mu\text{m}$ 、全粒子の内の 20% の粒径が $0.1 \mu\text{m} \sim 20 \mu\text{m}$

- 5 の範囲に属する膨張黒鉛とポリカルボジイミド樹脂とを表 6 に示す組み合わせで混合し、 150°C 、 100 kg/cm^2 の圧力で成型品を作った。この成型品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 6 に示す。

比較例 2

- 10 比較例 1 で使用した成型品を窒素ガス中で 1000°C まで焼成した。この焼成品を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 6 に示す。

比較例 3

- 平均粒径が $0.5 \mu\text{m}$ 、全粒子の内の 20% の粒径が $0.1 \mu\text{m} \sim 20 \mu\text{m}$ の範囲に属する膨張黒鉛とポリカルボジイミド樹脂とを表 6 に示す組み合わせで混合し、 150°C 、 100 kg/cm^2 の圧力で成型品を作った。この成型品
- 5 を用いて、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した結果を表 6 に示す。

表 6

	比較例 1	比較例 2	比較例 3
焼成温度 ($^\circ\text{C}$)	なし	1000	なし
膨張黒鉛	100	100	100
樹脂 (ポリカルボジイミド)	10	100	1000
密度	1.25	1.21	1.23
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)	0.2	1	0.3
加工性	良好	良好	脆く溝加工 できなかった

比較例 4

- 10 密度 2.0 g/cm^3 と 1.7 g/cm^3 のグラファイト材料にポリカルボジイミド樹脂を含浸し、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝加工性を測定した。結果を表 7 に示す。

比較例 5

溝加工を施した密度 1.7 g/cm^3 と 2.0 g/cm^3 のグラファイト材の表層に、ポリカルボジイミド樹脂を塗布し、窒素ガス雰囲気下で 1500°C で焼成し、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性を測定した。結果を表 7 に示す。

5

表 7

	比較例			
	比 4-1	比 4-2	比 5-1	比 5-2
焼成温度 ($^\circ\text{C}$)	なし	なし	1500	なし
密度	1.7	2	1.7	2
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)	90	0.4	9	4×10^{-5}
加工性	良好	良好	良好	良好

比較例 6

密度 1.5 g/cm^3 のガラス状カーボンを使用し、実施例 1 と同様にして固体高分子電解質型燃料電池用セパレータを製造した後、密度、ガス透過性、溝

10 加工性を測定した。結果を表 8 に示す。

表 8

比較例	比較例 6
焼成温度 ($^\circ\text{C}$)	なし
密度	1.5
ガス透過率 ($\text{cm}^3\text{cm}^{-2}\text{min}^{-1}\text{atmN}_2$)	1×10^{-7}
加工性	溝加工中に溝が欠けてしまった

産業状の利用可能性

- 本発明の固体高分子電解質型燃料電池用セパレータは、燃料電池のガス拡散電極間に挟まれる固体高分子電解質型燃料電池用セパレータであって、平均粒
- 5 径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物よりなり、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物中に膨張黒鉛粉末が分散されている炭素複合材料の片面又は両面に、酸化剤ガス又は燃料
- 10 ガス供給溝を形成したものであり、軽量で溝加工を容易に施すことができ、しかも高いガスバリア性を有する優れたものである。

請求の範囲

1. 燃料電池のガス拡散電極間に挟まれる固体高分子電解質型燃料電池用セパレータであって、平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物よりなり、熱可塑性樹脂、熱硬化性樹脂或いはその焼成物中に膨張黒鉛粉末が分散されている炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成したことを特徴とする固体高分子電解質型燃料電池用セパレータ。
- 10 2. 平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱可塑性樹脂又は熱硬化性樹脂を混合分散し、常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形して得られた炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成することを特徴とする固体高分子電解質型燃料電池用セパレータの製造方法。
- 15 3. 膨張黒鉛粉末と熱可塑性樹脂又は熱硬化性樹脂の割合が、膨張黒鉛粉末100重量部に対し、熱可塑性樹脂又は熱硬化性樹脂10乃至1000重量部である請求項2に記載の固体高分子電解質型燃料電池用セパレータの製造方法。
4. 平均粒径が $5\mu\text{m}\sim 12\mu\text{m}$ 、粉末全粒子の内の80%以上の粒径が $0.1\mu\text{m}\sim 20\mu\text{m}$ の範囲に属する膨張黒鉛粉末と、熱硬化性樹脂を混合分散し、
20 常温 $\sim 400^{\circ}\text{C}$ の温度下で加圧成形した後、該成形物を、非酸化性雰囲気下、

700℃～3000℃で焼成して得られた炭素複合材料の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成することを特徴とする固体高分子電解質型燃料電池用セパレータの製造方法。

5. 平均粒径が5 μm ～12 μm 、粉末全粒子の内の80%以上の粒径が0.

5. 1 μm ～20 μm の範囲に属する膨張黒鉛粉末と、熱硬化性樹脂を混合分散し、常温～400℃の温度下で加圧成形した後、該成形物の片面又は両面に、酸化剤ガス又は燃料ガス供給溝を形成し、非酸化性雰囲気下、700℃～3000℃で焼成することを特徴とする固体高分子電解質型燃料電池用セパレータの製造方法。

10. 6. 膨張黒鉛粉末と熱可塑性樹脂又は熱硬化性樹脂の割合が、膨張黒鉛粉末100重量部に対し、熱可塑性樹脂又は熱硬化性樹脂10乃至1000重量部である請求項4又は5に記載の固体高分子電解質型燃料電池用セパレータの製造方法。

7. 非酸化性雰囲気下での焼成を、1000℃～2500℃で行う請求項4又

15. は5に記載の固体高分子電解質型燃料電池用セパレータの製造方法。

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01859

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ H01M8/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996
Toroku Jitsuyo Shinan Koho	1994 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 01-154467, A (Hitachi, Ltd.), June 16, 1989 (16. 06. 89), Claims 1 to 3; page 3, lower right column, lines 13 to 19 (Family: none)	1 - 7
A	JP, 01-311570, A (Hitachi Chemical Co., Ltd.), December 15, 1989 (15. 12. 89), Claim 1; page 2, upper right column, line 12 to lower left column, line 1 (Family: none)	1 - 7
A	JP, 60-090807, A (Kobe Steel, Ltd.), May 22, 1985 (22. 05. 85), Page 5, upper left column, line 13 to upper right column, line 16; page 5, lower left column, lines 12 to 15 & DE, 3413646, A & US, 4582632, A	1 - 7
A	JP, 62-059508, A (Tokai Carbon Co., Ltd.), March 16, 1987 (16. 03. 87), Page 2, upper right column, line 14 to lower left column, line 1; page 5, lower right column,	1 - 7

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search

September 30, 1996 (30. 09. 96)

Date of mailing of the international search report

October 8, 1996 (08. 10. 96)

Name and mailing address of the ISA/

Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/01859

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>line 19 to page 3, upper left column, line 16 (Family: none)</p> <p>JP, 04-214072, A (Osaka Gas Co., Ltd.), August 5, 1992 (05. 08. 92), Paragraphs (0030) to (0031) (Family: none)</p>	1 - 7

国際調査報告

国際出願番号 PCT/J P 96/01859

A. 発明の属する分野の分類 (国際特許分類 (IPC))
Int. Cl.⁸ H01M8/02

B. 調査を行った分野
調査を行った最小限資料 (国際特許分類 (IPC))
Int. Cl.⁸ H01M8/02

最小限資料以外の資料で調査を行った分野に含まれるもの
日本国実用新案公報 1926-1996
日本国公開実用新案公報 1971-1996
日本国登録実用新案公報 1994-1996

国際調査で使用した電子データベース (データベースの名称、調査に使用した用語)

C. 関連すると認められる文献

引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	J P, 01-154467, A (株式会社日立製作所), 16. 6月. 1989 (16. 06. 89), 特許請求の範囲請求項1~請求項3, 第3頁下右欄13~19行目 (ファミリーなし)	1~7
A	J P, 01-311570, A (日立化成工業株式会社), 15. 12月. 1989 (15. 12. 89), 特許請求の範囲請求項1, 第2頁上右欄12行目~下左欄1行目 (ファミリーなし)	1~7
A	J P, 60-090807, A (株式会社神戸製鋼所), 22. 5月. 1985 (22. 05. 85), 第5頁上左欄13行目~上右欄16行目、第5頁下左欄12~15行目&DE, 3413646, A&US, 4582632, A	1~7

☒ C欄の続きにも文献が列挙されている。

☐ パテントファミリーに関する別紙を参照。

* 引用文献のカテゴリー

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30. 09. 96

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特許庁審査官 (権限のある職員)
吉水 純子

4 K 9444

電話番号 03-3581-1101 内線 3435

C (続き). 関連すると認められる文献		
引用文献の カテゴリー*	引用文献名 及び一部の箇所が関連するときは、その関連する箇所の表示	関連する 請求の範囲の番号
A	J P. 62-059508, A (東海カーボン株式会社), 16. 3月. 1987 (16. 03. 87), 第2頁上右欄14行目～下左欄1行目、第5頁下右欄19行目～第3頁上左欄16行目 (ファミリーなし)	1～7
A	J P. 04-214072, A (大阪瓦斯株式会社), 5. 8月. 1992 (05. 08. 92), 【0030】～【0031】 (ファミリーなし)	1～7